



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Declaration under 37 C.F.R. § 1.132

Group Art Unit: 1314

Primary Examiner: Hien Thi Tran

Title: Monolith Loop Reactors

Declaration of Dr. Thorsten R. Boger

I, Thorsten R. Boger, do hereby declare as follows:

1. I am a Chemical Engineer by profession, having received the following professional engineering degrees:

- a Dipl.-Ing. (Masters) Degree in Chemical Process Engineering from the University of Stuttgart, Germany in April of 1991; and
- a Dr.-Ing. (Doctorate) Degree from the Faculty of Process Engineering, the University of Stuttgart, Germany, in May of 1999.

Additionally, from 1991 to 1994 I held the position of Research Engineer in the Zentralabteilung für Forschung und Entwicklung (Central R&D) at Kraftanlagen AG of Heidelberg, Germany, and from 1994 to 1997 I held the position of Research Assistant in the Institut für Chemische Verfahrenstechnik (Department of Chemical Process Engineering) at the University of Stuttgart, Germany.

2. I joined Corning GmbH as a Chemical Engineer in April of 1997, and currently hold the position of Engineering Manager – Refining & Chemical Technologies in the Corning Environmental Technologies division of that company;

3. In the course of my employment with Corning I have been involved in the development of a number of technologies pertaining to catalyst substrates and catalytic reactors for applications in the fields of industrial emissions control and chemical processing. In particular, I have been involved in the development of catalysts and catalytic reactor designs for large-scale industrial processes.

4. I am the named inventor in the above-entitled application and I have been informed that some of the claims of that application stand rejected as unpatentable in light of U.S. Patent No. 6,086,832 (Ohta) and U.S. Patent No. 6,087,455 (Lange), Ohta being cited for a disclosure of a loop reactor using a pelletized catalyst and Lange for a disclosure of the use of a honeycomb catalyst in a moving bed reactor. I am further informed of the Examiner's finding that the use of a honeycomb catalyst as taught by Lange in the loop reactor disclosed by Ohta would not confer patentability on the claims of the above-entitled application, since it would involve a mere change in the shape of a component. The guiding principle cited by the Examiner to deny patentability is that such changes in shape are generally held to be within the level of ordinary skill in the art, absent the showing of unexpected results.

5. The data hereinafter set forth is offered to demonstrate that the results obtainable through the use of a monolith loop reactor in accordance with the invention are both superior to, and entirely unexpected from, the disclosures of Ohta and Lange. Further, those data will demonstrate the criticality of catalyst shape to the effective functioning of the monolith loop reactors presently claimed.

6. Ohta describes a laboratory testing device which comprises a reactor vessel into which a basket with a solid catalyst is placed and in which a rapid circulation is achieved by means of a stirrer. The system is capable of enabling tests in which the catalyst is exposed to a gaseous and a liquid reactant stream. A liquid recovery portion is provided in addition to the reactor vessel. The catalyst described in the examples is of pellet type (e.g. small trilobes, as used for example in hydroprocessing applications).

7. The invention of the above-entitled application includes a liquid processing apparatus in which a honeycomb monolith catalyst is disposed within a liquid containment vessel that is configured to also provide a passageway within the vessel allowing for the internal recirculation of a liquid medium repeatedly through the parallel channels of a honeycomb monolith catalyst. As this recirculation is achieved by means of a mechanical device (e.g. stirrer), a liquid agitation (e.g. a liquid jet) or gas bubbles added to the liquid, the resistance of the catalyst to liquid flow through the honeycomb catalyst is critical.

8. The data presented below, based on widely accepted principles of hydrodynamics, will demonstrate that the use of honeycomb monolith catalysts, rather than other catalyst shapes such as pellets or monolithic foams, is essential to reactor operability for commercial scale

loop reactors using these modes of liquid circulation, and that the use of such other catalyst shapes would prevent such a reactor from functioning.

9. As is well understood in the field chemical reactor design, each catalyst packing or structure presents a certain resistance to any fluid flow, this characteristic being commonly referred to as pressure drop. Besides hydrostatic contributions, which are similar for all structures, the resistance to flow is a result of momentum losses due to friction within the fluid and between the fluid and the surface of the solid structure(s), as well as to losses as a result of turbulence. These effects have been extensively analysed in the literature. Accordingly, pressure drop differences between monolithic honeycomb catalysts and foam monoliths or catalyst pellet beds under useful liquid flow conditions to be calculated from art-recognized sources such as the following:

- [1] Andrigo P., R. Bagatin, G. Pagani. *Catalysis Today* **52** (1999) 197-221
- [2] Richardson J.T., Y. Peng and D. Remue. *Applied Catalysis A: General* **204** (2000) 19-32
- [3] for example: Day J.P. SAE 971024
- [4] Ramachandran P.A., R.V. Chaudhari. *Three-Phase Catalytic Reactors*. Gordon and Breach Science Publishers. ISBN 0-677-05650-8
- [5] Correlations by Heiszwolf, J. et al.(TU Delft); Poster at Annual Conference of Dutch Chemical Engineers (2000)
- [6] Krishna R., J.M. van Baten. *Catalysis Today* **79-80** (2003) 67-75

10. Summarizing relevant principles from this literature, where only one fluid phase is present, the well-known Ergun equation from [1] above can be used for computations involving random packings (e.g. pellets, spheres or rings), while for foam structures the correlations and data given by Richardson et al. in [2] are applicable. For single-phase flow through honeycomb monoliths the standard correlation based on the Hagen-Poiseuille equation is used [3]. If two fluid phases are present the data for sphere or pellet packings can be generated from the correlation given in [4], while for honeycomb monoliths the correlation reported in [5] can be used with minor modifications based on internally generated experimental data. In all cases the pressure drop contributions of the inlet and outlet of the catalyst bed are generally neglected since they usually do not exceed a few percent.

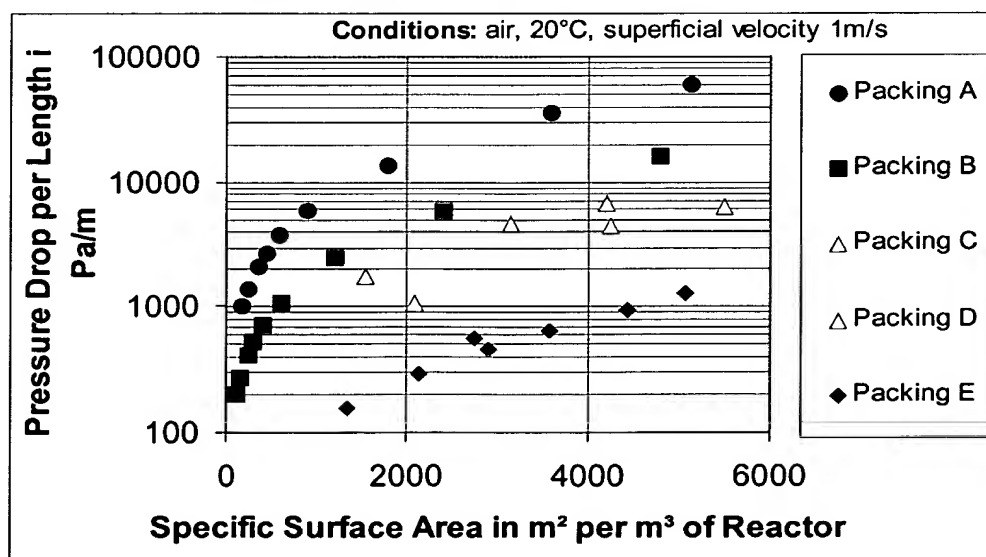
11. Table I below presents data concerning the geometries of comparable and conventional catalyst packings of pellet, foam and honeycomb monolith type that will hereinafter be characterized as to their respective pressure drop characteristics:.

Table I – Catalyst Geometries

Packing	A	B	C	D	E
Shape	Spheres	Rings	Ceramic Foam	Ceramic Foam	Honeycomb Monolith
Geometry	Diameter 0.5-20 mm	OD	10, 30, 45ppi (= 4, 12, 18 pores/cm)	10, 30, 45ppi (= 4, 12, 18 pores/cm)	50-1200 cpsi
Void Fraction	40%	60%	>80%	65%	~70-85%
Comment			Foam properties taken from [2]	Taken from [2], adjusted for lower void fraction.	Data for commercial products.

12. For the example of single-phase gas flow through a fixed catalyst packing bed, a standardized test condition can be established by flowing air through the catalyst bed at a temperature of 20°C, a pressure of 1 bar, and a superficial gas velocity of 1m/s. Fig. 1 below is a graph plotting catalyst bed pressure drop per unit length against the geometric surface area per fixed bed volume under this flow condition, for beds of each of the catalyst shapes characterized in Table 1 above. Geometric surface area is plotted as the key bed characteristic since for many reactions it directly reflects the functionality (i.e., the catalytic activity) of any solid catalyst.

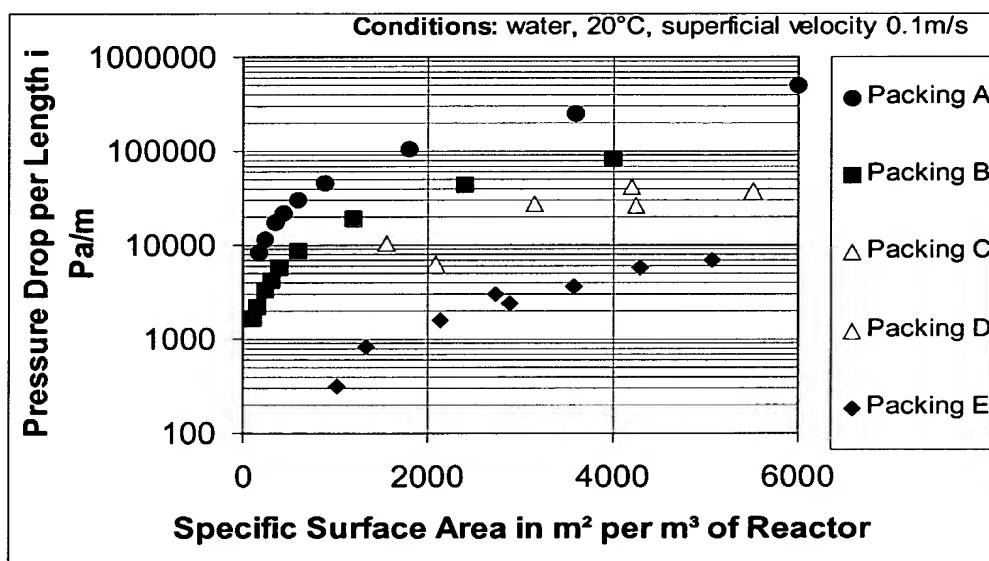
Fig. 1 - Gas Flow Through A Fixed Bed.



13. The data in Fig. 1 clearly indicate that the honeycomb monolith packing has a flow resistance more than one order of magnitude less than the flow resistance of any of the random packings, and 4 times less than even that of the most open foam monolith packing. This is because fluid flow within the straight channels of the monoliths remains laminar, but becomes turbulent for all the other packings.

14. For the case of liquid (single-phase) flow through a fixed bed, flowing water at a temperature of 20°C, a pressure of 1 bar, and superficial velocity of 0.1 m/s provides a useful standardized test condition. For each of the different catalyst shapes to be characterized from Table 1 above, Fig. 2 below presents the calculated data in plots of pressure drop per unit of catalyst bed length versus catalyst bed geometric surface area at equivalent fixed bed volumes.

Fig. 2 – Liquid Flow Through A Fixed Bed.



15. The results obtained for liquid flow shown in Fig. 2 parallel those observed for single phase gas flow, in that the pressure drop across the honeycomb catalyst bed is at least an order of magnitude less than those for the random packings, and significantly lower than those for either monolithic foam bed.

16. For two-phase gas-liquid flow through a fixed bed, a flowing water-air mixture at a temperature of 20°C and a pressure of 1 bar can be established as a useful standard for comparing bed characteristics. For this analysis, the comparisons between catalyst beds are

made on an equal geometric surface area basis, as appropriate for transport limited chemical processes, and are provided for two different sets of air-water flow conditions.

17. Table 2 below sets forth comparative data for pellet (spherical) catalyst beds and honeycomb monolith catalysts at two different levels of bed geometric surface area, approximating 2000 and 4000 m²/m³, respectively. Sphere geometries are reported as sphere diameters, in mm, and honeycomb geometries as cell densities/channel wall thicknesses, in cells/inch² of honeycomb cross-section and thousandths of an inch (mils), respectively. Bed pressure drops are reported in units of Pascals/meter, and gas and liquid flow velocities in meters/second. As is apparent from the data in Table 2, honeycomb monolith catalysts present significantly lower pressure drops than do standard pelletized catalysts for two-phase gas-liquid process streams, just as they do for single-phase gas and liquid process streams.

Table 2 – Gas-Liquid Flow Through Fixed Beds

Packing	Geometry	Geometric Surface Area m ² /m ³ of bed	Pressure Drop per Length in Pa / m at	
			$u_{G0} = 0.05\text{m/s}, u_{L0}=0.10\text{m/s}$	$u_{G0} = 0.01\text{m/s}, u_{L0}=0.03\text{m/s}$
Spheres	ϕ 1.8mm	2000	57,600	3,700
Honeycomb	230/7	2135	4,100	820
Spheres	ϕ 0.9mm	4000	136,000	7,850
Honeycomb	900/3	4300	10,100	2,400

Note: u_{G0} ...superficial gas velocity, u_{L0} ...superficial liquid velocity.

Monolith geometry notation: cell density in cpsi / wall thickness in 1/1000inch

As also apparent from the data in Table 2, honeycomb monolith catalysts present significantly lower pressure drops than do standard pelletized catalysts for two-phase gas-liquid process streams, just as they do for single-phase gas and liquid process streams.

18. A correct analysis of pressure drop data such as presented above in Table 2 above is required to understand the unexpected benefits of the fixed honeycomb catalyst bed design for internal loop reactors such as described in the above-entitled patent application. The driving forces that can be effectively applied to force liquid recirculation through the catalyst beds in loop reactors are practically limited, both for mechanical reasons and because at higher forces the flowing liquid can simply by-pass the bed via internal liquid recirculation passageways. Given a practical limit on the driving force, the use of a catalyst bed with a pressure drop that exceeds the pressures available for liquid recirculation would result in poor utilization of the bed. A maximum practical limit on catalyst bed pressure drops useful for internal loop

reactors such as described in the rejected claims, i.e., that utilize mechanical (stirrer), gas bubble or liquid jet means for liquid recirculation within the reactor, is about 500 Pa/m.

19. In light of this limitation, a further important evaluation of catalyst bed performance relates to the maximum liquid recirculation rates that can be reached before the practical limit on catalyst bed pressure drop for any chosen loop reactor design is exceeded. Table 3 below sets forth data respecting the maximum liquid flow rates possible through catalyst beds of both pelletized and honeycomb monolith design while not exceeding a maximum pressure drop value of 500 Pa/m. The liquid flow rates are presented in terms of effective liquid velocity through the beds. The basis of the performance comparisons presented in Table 3 is again a gas-liquid feed stream comprising air and water at a temperature of 20°C and a pressure of 1 bar. In order that the effects of varying liquid flow only through the beds can be determined, the gas flow rate is fixed to maintain a superficial gas velocity of 0.03m/s through the bed.

20. Table 3 compares fixed beds made up of pelletized (spheres) and honeycomb packings at bed surface area levels of about 2000 m²/m³ and about 4000 m²/m³. The performance parameter selected to reflect the liquid recirculation performance is the effective linear velocity of liquid flow through the bed that can be reached without exceeding the 500Pa/m pressure drop threshold. The geometries and geometric surface areas of the catalyst beds are reported on the same basis and in the same units as reported above in Table 2, while the liquid linear velocities are reported in meters/second.

Table 3 – Maximum Liquid Flows Through Fixed Beds

Packing	Geometry	Geometric Surface Area m ² /m ³ of bed	Maximum Liquid Flow for <500Pa/m u _{Lo} in m/s
Spheres	φ 1.8mm	2000	0.00045
Honeycomb	230/7	2135	0.01300
Spheres	φ 0.9mm	4000	0.00015
Honeycomb	900/3	4300	0.00365

Note: u_{G0}...superficial gas velocity set to 0.03m/s, u_{Lo}...superficial liquid velocity.

Monolith geometry notation: cell density in cpsi / wall thickness in 1/1000inch

21. From a study of the data presented in Table 3 it is evident that the liquid recirculation rates attainable through pelletized catalyst beds operating below the pressure drop limit are much lower than those achievable with honeycomb monoliths of substantially the same geometric surface area. These results are largely attributed to the higher levels of turbulence

in the pelletized bed, but in any case it is clear that, with randomly packed pellet beds only extremely low liquid flow rates are possible. This is in fact the main reason why large pellet bed loop reactors are not used on an industrial scale today.

22. In summary, the foregoing data clearly indicate the critical importance of catalyst shape on the operating effectiveness of the monolith loop reactors of the invention. Yet I find no reference to these effects in either of the patents relied on in support of the rejection of the claims of the above-entitled application. Accordingly I have concluded that neither the criticality of catalyst shape nor the unexpected effectiveness of honeycomb monoliths for use in internal loop reactors is suggested by the cited prior art, or any other prior art of which I am aware.

Having first been informed that wilful false statements made herein may jeopardize the validity of any patent issuing on the above entitled application and may be punished by fine, imprisonment, or both under 18 U.S.C. 1001, I hereby declare that all statements made herein of my own knowledge are true, and all statements made on information and belief are believed to be true.

Signed:



Thorsten R. Boger

Date: 9 / 5 / 03